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MAGNETIC PHASE TRANSITIONS IN IRON AND NICKEL PHOSPHORUS TRICHALCOGENIDES *

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ABSTRACT

The magnetic phase transitions in layered transition-metal phosphorus trichalcogenides (MPX_3; M = Fe, Ni and X = S, Se) were investigated using differential scanning calorimetry (DSC). The transition enthalpy and temperature were measured; the results are discussed and compared with previous literature data obtained using other techniques.

INTRODUCTION

Iron and nickel phosphorus trichalcogenides are layered materials with monoclinic ($FePS_3$ and $NiPS_3$) or rhombohedral ($FePSe_3$) crystallographic unit cells [1,2]. Chalcogen layers are stacked in an ABC sequence in the monoclinic trisulphides and in an AB sequence in the rhombohedral triselenide. The planes of pseudo-octahedral sites between two chalcogen layers are alternatively empty (van der Waals gap) or occupied by phosphorus dimers and metal cations. Lithium ions can be intercalated in the van der Waals gap and this property has been exploited successfully in the fabrication of new lithium batteries [3].

These compounds have also attracted a considerable interest for their quasi-bidimensional [2-D] magnetic properties. In transition metal phosphorus trichalcogenides, the metal cations are arranged in a honeycomb lattice in the *ab* plane. At low temperatures an antiferromagnetic order arises with ferromagnetic chains coupled to each other antiferromagnetically in the *ab* plane. Interplanar nearest-neighbour chains are coupled ferromagnetically in $NiPS_3$ and antiferromagnetically in the iron compounds [4,5].

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* Dedicated to Professor Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

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Among the effects observed around the Néel temperature (T_N), one of the most intriguing is the strong spin-dependent phonon Raman scattering in iron phosphorus trisulphide [6]. Two strong narrow peaks and a weaker one are activated in the 80–120 cm^{-1} region in the Raman spectrum of the magnetic phase, and some phonon peaks at higher frequencies are enhanced. On the contrary, the phonon Raman spectrum of iron phosphorus triselenide is almost completely unaffected by the magnetic ordering [6], and that of nickel phosphorus trisulphide exhibits only peak enhancements and the appearance of a broad band in the 200–900 cm^{-1} region [7].

The appearance of new phonon lines in the $FePS_3$ spectrum is very likely to originate from the folding of phonon branches in the Brillouin zone, due to the doubling of the unit cell along the *a*- and *c*-axis below the magnetic ordering temperature [6]. It is worth pointing out, however, that the crystal symmetry of $FePS_3$ does not change around T_N.

The activation of sharp phonon peaks in the ordered magnetic phase was also observed in vanadium di-iodide [8] and in europium chalcogenides [9]. All these compounds exhibit first-order magnetic transitions [10,11].

This article reports on the study of the magnetic phase transitions in $FePS_3$, $FePSe_3$ and $NiPS_3$ by differential scanning calorimetry (DSC). The transition temperatures were evaluated and the enthalpies of transition were measured. The thermal behaviour of these materials is discussed taking into account the previous literature data obtained with different experimental techniques.

EXPERIMENTAL

The samples were taken from flat single crystals (about 5 × 5 × 0.1 mm) of $FePS_3$, $FePSe_3$ and $NiPS_3$, grown in a two-zones furnace from the pure elements, as described in more detail in ref. 4. The starting materials were the following: Fe (99.5%), Ni (99.99%), P (99.999%) and S (99.99%) (all supplied by Koch Light), and Se (99.999%) (supplied by Prolabo). With regard to the single crystal stoichiometry, microprobe elemental analysis of the trisulphides showed that the difference between the expected and measured content of each element did not exceed 1%, which can be considered as satisfactory [12].

DSC measurements were carried out by means of a Perkin–Elmer model DSC-2 differential scanning calorimeter. The instrument was calibrated at heating rates of 5, 10 and 20 K min^{-1} with the following substances: cyclopentane (Fluka, puriss. 99.5%), mercury (C. Erba, R.P.-ACS) and gallium (Fluka, puriss. 99.999%). The purge gas was pure helium. For each compound, three samples, weighing 13–27 mg and tightly sealed in volatile sample pans of aluminium, were examined in the temperature range 100–300 K. For each sample at least three cooling and heating cycles were carried out. Cooling and heating rates were usually 10–20 K min^{-1} and 5–10 K min^{-1} respectively. Under these conditions, the DSC traces were reproducible and the observed peaks did not exhibit significant hysteresis upon cooling.

RESULTS AND DISCUSSION

An example of the DSC scans of $FePS_3$, $FePSe_3$ and $NiPS_3$ around the magnetic ordering temperature is illustrated in Figs. 1–3, respectively, and the transition enthalpy and Néel temperature values are summarized in Table 1.

An endothermic peak is clearly observed in the $FePS_3$ trace. It exhibits a 'lambda' shape with a shoulder on the low temperature side. A transition temperature of about 118 K has been estimated from the onset of the λ-peak, while the heat of transition, evaluated by graphical integration after drawing a smooth curve under the λ-peak, is about 390 J mol^{-1} (Fig. 1).

The endothermic peak detected on $FePSe_3$ is weaker and more symmetric (Fig. 2), corresponding to a transition temperature of 106 K and to a heat of transition of about 120 J mol^{-1}. In this compound, there was also a step in the DSC curve at $T \simeq 180$ K.

$NiPS_3$ is characterized by a different behaviour. A small hump in the slope of the curve is observed between 145 and 157 K (Fig. 3). The area corresponding to this hump is smaller than that of the iron compounds, the heat of transition being about 29 J mol^{-1} in this case.

The Néel temperatures of iron and nickel phosphorus trichalcogenides have been measured with different techniques, including magnetic susceptibility [13], NMR [14], XRD and Mössbauer spectroscopy [15]. Owing to different definitions of the transition temperature, as well as variation in the

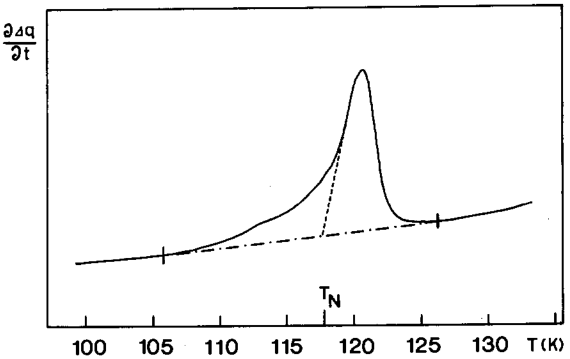

Fig. 1. Heating run of $FePS_3$ (scan rate 10 K min^{-1}).

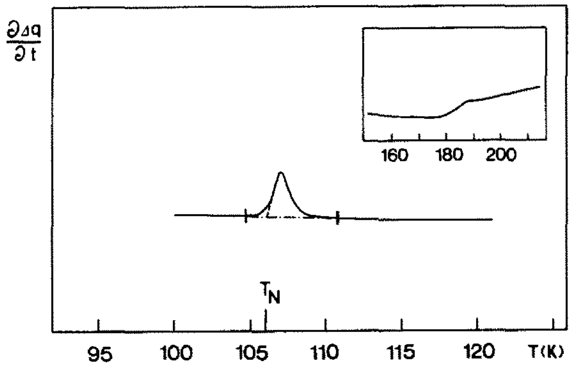

Fig. 2. Heating run of $FePSe_3$ around T_N (scan rate 5 K min^{-1}). The inset shows the heat capacity step around 180 K.

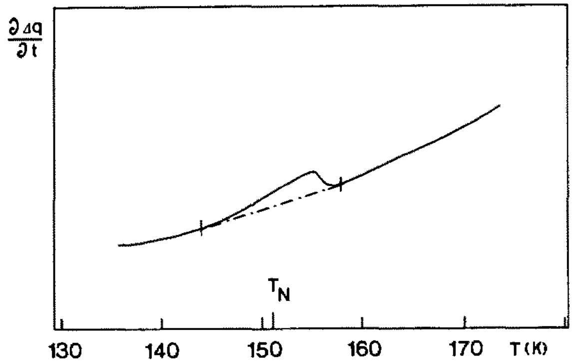

Fig. 3. Heating run of $NiPS_3$ (scan rate 10 K min^{-1}). The *y*-scale is magnified 2.5 times with respect to Figs. 1 and 2.

TABLE 1

Magnetic transition temperatures and enthalpies for iron and nickel phosphorus trichalcogenides

	T_N (K)		ΔH (J mol^{-1})
	Present work	Literature	
$FePS_3$	118 ± 1	116 (14), 120 (5)	390 ± 10
$FePSe_3$	106 ± 1	112 (14), 119 (5)	120 ± 20
$NiPS_3$	151 ± 1	155 (14)	29 ± 1

calibration methods and in sample quality, the reported values are slightly scattered. For $FePS_3$ and $FePSe_3$, T_N values were reported in the 116–120 K and 112–119 K ranges, respectively. For $NiPS_3$, the most reliable T_N value seems to be that obtained by NMR, namely 155 K [14]. In fact the sudden

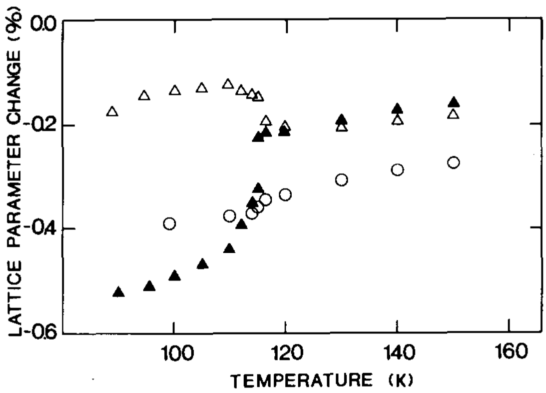

Fig. 4. Lattice parameter changes with respect to room temperature values versus temperature in $FePS_3$ (from ref. 15). Closed and open triangles and open circles indicate *a*, *b* and *c* lattice parameters, respectively.

disappearance of the ^{31}P NMR line, owing to the hyperfine field on the phosphorus atoms arising in the ordered magnetic phase, is very likely to be the best probe to measure T_N. With this technique, Chabre and coworkers found Néel temperatures for $FePS_3$, $FePSe_3$ and $NiPS_3$ of 116 K, 112 K and 155 K, respectively [14]. The results obtained in the present work are in reasonable agreement with those reported in the literature.

Powder XRD measurements at varying temperatures showed that in $FePS_3$ [15] and $NiPS_3$ [13] there is no change in the crystal symmetry at the magnetic transition, whereas in the iron compound, an abrupt change of the lattice parameters occurs. The *a*-axis decreases about 0.2% (with respect to the room temperature value) and the *b*-axis increases about 0.05% around T_N, whereas the *c*-axis contraction is monotonic and does not show any abrupt change (Fig. 4). On the contrary, the lattice parameters of $NiPS_3$ show a monotonic decrease as the temperature lowers to around T_N [13]. Unfortunately, no data are available, as far as we know, on the temperature dependence of the $FePSe_3$ lattice parameters.

XRD and DSC data seem to be well correlated and consistent with a first-order magnetic transition in $FePS_3$ and a second-order transition in $NiPS_3$. In $FePS_3$, a relatively high enthalpy of transition is measured with respect to the other MPX_3 compounds and magnetostriction effects were observed [15], whereas a low heat of transition and no abrupt change in lattice parameters were measured on $NiPS_3$ [13].

An intermediate behaviour characterizes $FePSe_3$. The peak around 106 K is similar to that observed in the trisulphide, but it is less intense and more symmetric. As suggested by Jernberg et al. [15], a first-order transition may also occur in the triselenide, but the magneto-elastic coupling is weaker and small lattice parameter changes are expected around the paramagnetic–antiferromagnetic phase transition.

A first-order magnetic transition, which is characterized by a sharp peak in heat capacity and by an abrupt change in the sample density [16], is indicative of exchange interactions strongly dependent on the interatomic distances and of strong magneto-elastic couplings. Vanadium di-iodide, europium selenide and telluride, which exhibit new, strongly activated phonon lines in the Raman spectrum of the ordered phase, are characterized by a first-order transition around T_N [10,11]. Together with the appearance of a magnetic superstructure, the first-order character of the transition, i.e. the presence of strong magneto-elastic couplings, seems to be a necessary condition for the observation of zone boundary phonon Raman scattering in the magnetic phase.

In conclusion, the results of the present DSC investigation are consistent with the available XRD and Raman data on transition-metal phosphorus trichalcogenides, supporting the idea of a first-order magnetic transition in $FePS_3$ and perhaps in $FePSe_3$, and suggesting that the magnetic transition in $NiPS_3$ is of the second order. In particular, the larger heat of transition, the abrupt change in the lattice parameters and the activation of zone boundary phonon lines in the Raman spectrum of the antiferromagnetic ordered phase are indicative of larger magneto-elastic couplings in $FePS_3$ compared with $FePSe_3$ and $NiPS_3$.

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